PREPARATION OF BIODIESEL FROM WASTE COOKING OIL VIA TWO STEP BATCH CATALYZED PROCESS WITH THE AID OF ACID SULFURIC AND SODIUM HYDROXIDE AS THE CATALYST

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor in Chemical Engineering

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MAY 2008

I declare that this thesis entitled “Preparation of biodiesel from waste cooking oil via two step batch catalyzed process” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently in candidature of any other degree.

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Date : 14 MAY 2008

Special dedication to:
For my beloved family.

Wan Abd Ghani Bin Wan Salim

Siti Rokiah Bt Omar

Wan Ahmad Kamal Bin Wan Abd Ghani

Wan Julia Bt Wan Abd Ghani

Wan Julina Bt Wan Abd Ghani

Wan Jasreen Bt Wan Abd Ghani

Thank you for everything…..

I love all of you so much….

ACKNOWLEDGEMENT

Alhamdulillah, grateful to Allah s.w.t., to give me the opportunity to complete my project report. First and foremost, I would like to thank our supervisor, Miss Sumaiya Bt Zainal Abidin@Murad for her endless supports and ongoing guidance throughout the course of this project ever since day one.I have acquired so much knowledge and experience from you. Words alone are insufficient to express our ultimate gratitude.

To all the lecturers of Faculty of Chemical and Natural Resources Engineering, thank you very much for sharing with us precious tips Friends are our pillar of inspirations and strength. Looking back, the obstacles, the sleepless nights, the verge of giving ups, the impossibilities and the arguments, are definitely worthwhile once I have completed this valuable project. I am also grateful to all my family members. I would like to thank my dearest family, parents, brother, sisters, and to whom I dedicated this dissertation. They always have been behind me with love, support and endless patient.

Thank you.

ABSTRACT

With environmental and energy source concerns on the rise, using agricultural fats and biological sources as fuel in diesel engines has captured increasing attention. Biodiesel has many advantages relative to petroleum. It has several processes that can be used in producing biodiesel but transesterification is the most commonly used in industry. In transesterification, it involved reaction between tryglycerides from waste cooking oil and methanol to produce biodiesel. The catalysts used in this experiment were acid sulfuric and sodium hydroxide catalyst. Two step catalyzed was chosen to be used in preparation biodiesel from waste cooking oil because the free fatty acid content was high in waste cooking oil. For the first step, the molar ratio used was 10:1 with the presence of 2 wt% of H_2SO_4 as catalyst with the temperature was 95^{o}C and 4 hours of reaction time. For the second step, the molar ratio used was 6:1 with the presence of 0.2, 0.4, 0.6, 0.8 and 1wt% of NaOH as catalyst with the temperature were 40,50,60,70,
80 ^{o}C and 1 hour of reaction time. Then, the biodiesel have to analyse by titration method to check free fatty acid and acid value content. It is proved that, this method can remove both free fatty acid and acid value up to 95%. This study also has indicated that the main factors that affect the reaction are reaction temperature and catalyst concentration.

ABSTRAK

Kesedaran tentang kepentingan alam sekitar telah membawa kepada penggunaan enjin diesel dari sumber semulajadi. Biodiesel boleh dihasilkan dari pelbagai cara. Dalam proses transesterifikasi, ia melibatkan tindakbalas antara *tryglycerides* dari minyak masak terpakai dan alkohol seperti metanol untuk menghasilkan biodiesel. Mangkin yang digunakan dalam eksperimen ini adalah asid sulfurik dan natrium hidroksida. Dua langkah mangkin telah dipilih untuk digunakan dalam pembuatan biodiesel dari minyak terpakai kerana kandungan bebas asid lemak adalah lebih tinggi dalam minyak masak terpakai. Bagi langkah pertama, nisbah molar yang digunakan adalah 10:1 dengan kehadiran 2 wt% H_2SO_4 sebagai mangkin dan suhunya adalah 95^oC serta tempoh tindakbalas adalah 4 jam. Bagi langkah kedua, nisbah molar yang digunakan adalah 6:1 dengan kehadiran 0.2, 0.4, 0.6, 0.8 and 1wt% of NaOH sebagai mangkin dan suhunya adalah 40,50,60,70,80^oC serta tempoh tindakbalas adalah 1 jam. Selepas pembuatan biodiesel,analisis seperti kandungan bebas lemak dan nilai asid diperlukan. Melalui analisis yang dijalankan,telah terbukti bahawa kaedah ini dapat menyingkirkan kandungan bebas lemak dan nilai asid lebih dari 95%.Kajian ini juga menunjukkan bahawa dua faktor penting yang mempengaruhi tindakbalas adalah suhu tindakbalas dan kepekatan mangkin yang digunakan.

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LIST OF SYMBOLS

g	-	gram
mL	-	mililitre
L	-	Litre
^{o}C	-	degree Celcius
%	-	percent
µl	-	microlitre
w/w	-	weight per weight

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CHAPTER 1

INTRODUCTION

Bioenergy, derived from sustainable agricultural practices and resources, has received increased consideration as a renewable substitute for fossil fuels. According to the World Energy Outlook by 2030 world energy consumption under the "Business as Usual" will increase by about 1.8% per year between 2000 and 2030. Bioenergy production being a compound issue that depends on many varying factors can play a significant role in improving rural productivity, energy supply, the environment, economic development and sustainability.

Bioenergy resources such as biofuels comprising of bio-ethanol and bio-diesel, biogas and biomass are derived from a variety of agricultural crops such as sugar cane, rapeseed coconut, Jojoba, Jatropha, palm oil, soybean and sunflower. As most of the crops used for biofuels are grown predominantly in developing countries, they hold the great potential for boosting these producing countries' trade, investment and development. Malaysia in practicing sustainable forest and crop management is unlikely to sacrifice its pristine forests to increase the area for producing palm oil for biofuel.

1.1 Background of study

Biodiesel is a clean-burning alternative fuel, produced from renewable resources such as vegetable oils and animal fats that are usually produced by a transesterification, reaction of vegetable or waste oil respectively with a low molecular weight alcohol and short chain alcohol, such as methanol and ethanol. During this process, the triglyceride molecule from vegetable oil is removed in the form of glycerin.

Palm oil, often said to be God's gift to Malaysia and Malaysia's gift to the rest of the world, certainly has the advantage over other vegetable oils in the production of bio-diesel.The Malaysian government is refocusing the use of palm oil to the production of biodiesel due to the huge demand from European countries that has encouraged the building of biodiesel plants. Strong demand for biodiesel from Europe as well as Colombia, India, South Korea and Turkey has fueled the industry's growth as more countries seek to reduce their reliance on fossil fuels. Malaysia has already begun preparations to change from diesel to bio-fuels by 2008, including drafting legislation that will make the switch mandatory. From 2007, all diesel sold in Malaysia must contain 5% palm oil. Being the world's largest producer of crude palm oil, Malaysia intends to take advantage of the rush to find cleaner fuels.

World production of palm oil in 2003 and 2004 rose by 3% to 28.13 million metric tons from 27.21 million in 2002 and 2003. Palm oil is the world’s second largest vegetable oil crop, running only slightly below soybean oil production of 31.98 million metric tons in 2003/4. The large production year in 2003 and 2004 for palm oil outpaced demand and that led to an 11% increase in stocks to 2.31 million metric tons from 2.09 million in 2002/3, although that is still a relatively tight stocks level compared to the 1999 to 2002 period. The world’s largest producer of palm oil by far is Malaysia with 48% of world production and Indonesia is the second largest producer with 36% of world production. Together they account for 84% of world production. Malaysian production in 2002 and 2003 rose by 6% to 12.520 million metric tons from 11.856 million in 2001/2. Indonesian production in 2002/3 rose by 8% to 9.480 million metric tons from 8.790 million in 2001/2. Figure 1 shows that the total consumption of palm oil in 2004

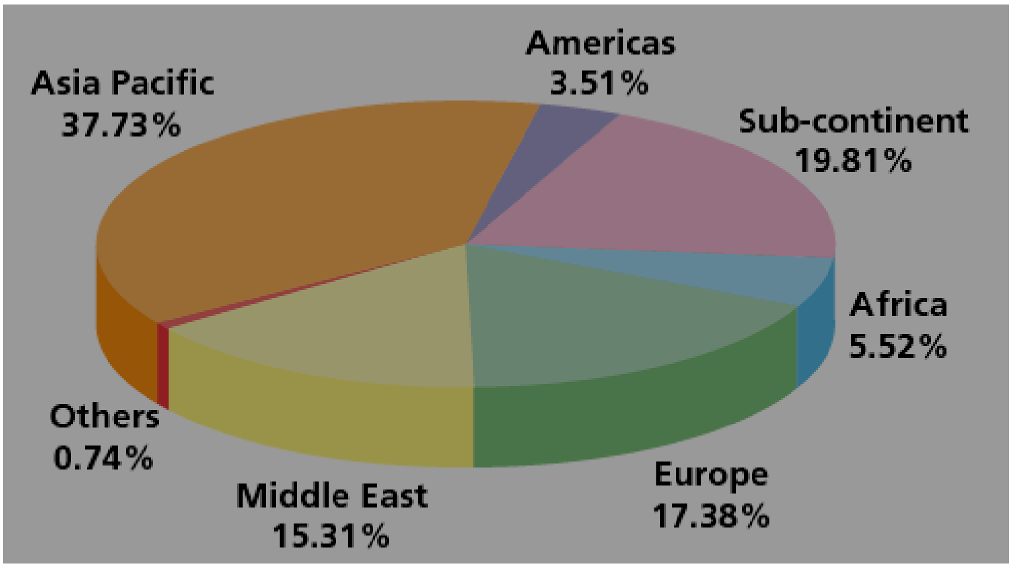

Figure 1: Total consumption of palm oil in 2004 (source: MPOB)

1.2 Objectives

To study the effects of catalyst concentration, reaction time and temperature on the two steps catalyze transesterification process in producing biodiesel

1.3 Scope of study

a) To study the effect of reaction temperature and catalyst concentration on methyl ester (biodiesel) yield.
b) To study the effect of reaction temperature and catalyst concentration on free fatty acid content.

c) To study the effect of reaction temperature and catalyst concentration on acid value.

1.4 Problem statement

Recently, increasing in crude oil prices and environment concerns about pollution from the car gases because the needs for alternative fuels that is more environmental friendly. Vehicles engines can contribute to the main pollutants when injected fuel does not find the necessary air for the complete combustion. These main primary pollutants such as carbon oxides, nitrogen oxides, alcohols, aldehydes, ketones, sulfur compounds and hydrocarbons can react with each other or with the sunlight to produce secondary pollutants like ozone that can be harmful to the environment.

Among different possible resources, diesel fuels from biological sources have shown great potential as substitutes for petroleum-based diesel fuels. Biodiesel that is produced from vegetable oils can be used as an alternative diesel fuels because its properties are similar to the conventional diesel. Other biological sources such as vegetable oil, soybean oil and animal fats, waste cooking oil also can be the raw material for biodiesel production. Waste cooking oil can cause environment pollution if not suitable treatment available when it is discharged. But, recently, it was found that waste cooking oil can be good commercial choice to produce biodiesel. Waste cooking oil gives interesting properties because it can be converted to biodiesel and waste cooking oil is available with low prices compared to fresh vegetable oil.

In our research, we have chosen two-step catalyzed transesterification process to improve the yield of biodiesel by the waste cooking oil. Biodiesel produced by transesterification reactions can be catalyzed with acid, alkali or enzyme. But, the former two types have received more attention due to their short reaction time and have lower cost. When free fatty acid content was lower than 0.5%, the sulfuric acid was drained and solid alkali was introduced into the system to complete the transesterification.

But, long reaction time, no recovery of catalyst and high cost of reaction equipment were disadvantages of this process. In addition to biodiesel, transesterification also yields glycerol as a valuable by-product for the pharmaceutical and cosmetics industry.

CHAPTER 2

LITERATURE REVIEW

2.0 General Overview

The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources to overcome these problems and preserving the global environment. Also, the need to search the alternative diesel fuels arises mainly from the concern about long term supplies of conventional hydrogen-based diesel fuels. Among the different possible sources, biodiesel that is manufactured from biological sources such as vegetable seed oil, soybean oil and some recovered animal fats present a promising alternative to substitute diesel fuels. It is becoming important position as an environmentally friendly substitute of diesel fuel in the markets of developed countries as well as developing one .Biodiesel or fatty acid alkyl esters chemically simple and defined as a "additive to diesel fuel that is derived from the oils and fats of plants and animals "or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat (ASTM). "Bio" represents its renewability and biodegradability in contrast to traditional petroleum-based diesel fuel. "Diesel" refers its use as fuel for diesel engines. In this context, it can be used in diesel engines and heating systems [Mittlebach *et al*., 1983; Staat and Vallet, 1994]

Biodiesel has many advantages compared to diesel fuel. The most important are the reduction of greenhouse effect and emissions from gas combustion. Biodiesel, which has low emissions profiles, is considered to be more sustainable and 'environmentally-friendly' than conventional diesels because the bio-component of these fuels is a biodegradable, nontoxic and clean renewable fuel with properties similar to conventional diesel. Historically, the use of neat biodiesels, particularly unrefined vegetable oils, and 'bio-rich' biodiesel (≥B40) blends has been associated with reduced vehicle or engine performance, such as impeded fuel flows, blocked fuel filters and fouled injectors and piston chambers [Bagby, 1987; Knothe *et al*., 1992; Graboski and McCormick, 1998 and references therein; Srivastava and Prasad, 2000].In addition, biodiesel does not required engine modification and have lower carbon monoxide releases to the atmosphere and hydrocarbon emissions than petroleum-based diesel fuels when burned. Biodiesel can become an excellent alternative fuel for diesel engine it is free from aromatic compounds and sulfur.

However, the cost of biodiesel is high due to the high cost of raw material (about 70-75% of the total cost) and high production cost involved, though this fuel has been developed about three decades [Hanna.,1999, Allen *et.a.l* 1999, *Leunc.,2001*]. So, biodiesel is not commonly used in daily life. The viscosity of vegetable oils is 10-20 times higher than of petroleum fuel, therefore using directly vegetable oils as a fuel can cause engine problems like injector fouling and has some drawbacks such as deposits at the injection system with consequent plugs or low atomization, hardening of seals, and low lubricating properties. One limitation to the use of biodiesel is its tendency to crystallize at low temperatures below $0^{o}C$. Methyl and ethyl esters of vegetable oils will crystallize and separate from diesel at temperatures often experienced in winter time operation. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operation. Another method to improve the cold flow properties of vegetable oil esters is to remove high-melting saturated esters by inducing crystallization with cooling, a process known as winterization

2.1 Renewable resources as the raw material for biodiesel

Among the different possible resources, diesel fuels derived from triglycerides have shown potential as substitutes for petroleum-based diesel fuels [Fukuda, Kondo, Nuda., 2001]. The use of animal fats and vegetable oils, such as palm, soya bean, sunflower, peanut olive oils, waste cooking oil, as alternative fuels for diesel engines have been studied and the rapid decline in crude oil reserves. But, the high cost of the fresh vegetable oil, waste cooking oil gives interesting properties because it can be converted to biodiesel and available with relatively cheap price [Nisworo, 2005; Zhang et al., 2003].

2.1.1 Animal fats

Currently, biodiesel is produced from a number of products, including soy bean oil, cotton seed oil, and yellow grease, among other things. Turning animal fat into biodiesel is not new. Animal fat begins to turn cloudy at a higher temperature than soybean biodiesel which also means that it could thicken up when it gets to a temperature lower than about 40 degrees Fahrenheit. Biodiesel production costs about a dollar more per gallon than conventional diesel.

2.1.2 Vegetable Oil

Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine). These include carbon deposits oil ring sticking and lubricating problems. Biodiesel produced from vegetable oils can be used as an alternative diesel fuels because its characteristics are almost the same to those of petroleum-based diesel fuels. For example, they have a similar viscosity with petroleum-based diesel fuel, their volumetric heating values are little lower, but they have high cetane and flash points [Fukuda, Kondo, Nuda., 2001]**.** The basic constituent of vegetable oils is triglyceride. Figure 2 shows a typical triglyceride molecule. Vegetable oils comprise 90 to 98% triglycerides and small amounts of mono- and diglycerides.

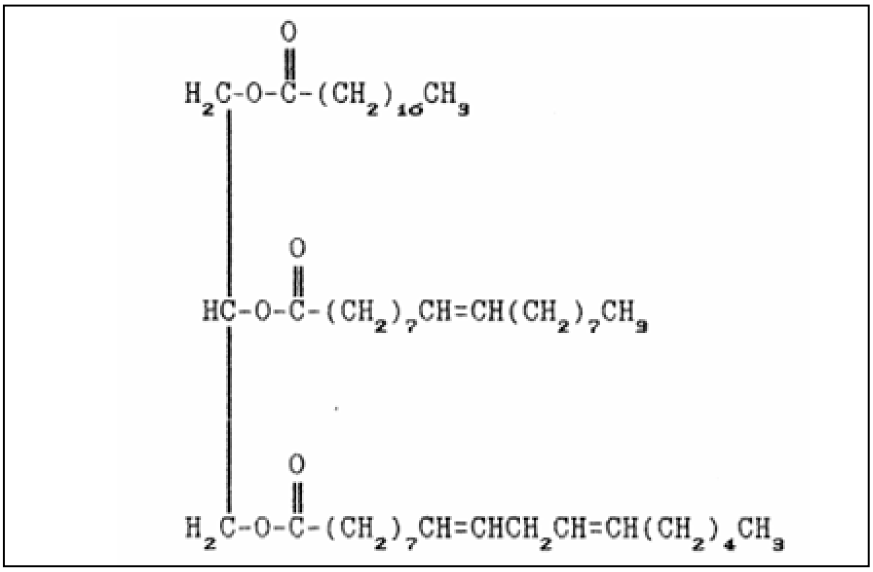

Figure 2.1: Structure of typical triglyceride molecules

Triglycerides are esters of three fatty acids and one glycerol. These contain substantial amounts of oxygen in its structure. Fatty acids vary in their carbon chain length and in the number of double bonds. The structures of common fatty acids are given in Table 1 [5]. Tables 2.2 summarize the fatty acid composition of some vegetable oils [Goeing, Schwab, Pyrde *et. al*., 1982; Kapur, Bhasin, Mathur., 1982]. The fatty acids which are commonly found in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic. Vegetable oils contain free fatty acids (generally 1 to 5%), phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds and traces of water [Markley; 1960].

Table 2.1 Chemical structure of common fatty acids

Fatty acid	**Systematic name**	**Structure**	**Formula**
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_{24}$
Myristic	Tetradecanoic	14:0	$C_{14}H_{24}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docoasanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	*cis*-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9, *cis*-12-octadecenoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9-*cis*-12,*cis*-15-octadecatrinoic	18:3	$C_{18}H_{30}O_2$
Erucic	*cis*-13-Docosanoic	22:1	$C_{22}H_{42}O_2$

Table 2.2 Chemical composition of vegetable oils

Vegetable oil	Fatty acid composition %									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cotttonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	0	1	19	59	9	7
Linseed	0	5	2	0	1	0	20	0	18	55
Peanut	0	11	2	1	0	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Sunflower	0	9	2	0	0	0	12	0	78	0
H_2O_2 sunflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesane	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0

The modified engines that have been built by Elsbett in Germany and Malaysia and Diesel Morten und Geratebau GmbH (DMS) in Germany and in USA show a good performance when fuelled with vegetable oils of different composition and grades [Krawczyk;1996].

2.1.3 Virgin Oil

Pure plant oil (PPO) (or Straight Vegetable Oil (SVO)), also, can become a raw material in producing biodiesel. In contrast to waste vegetable oil, is not a byproduct of other industries, and thus its prospects for use as fuels are not limited by the capacities of other industries. Production of vegetable oils for use as fuels is theoretically limited only by the agricultural capacity. For engines designed to burn diesel fuel, the viscosity of vegetable oil must be lowered to allow for proper atomization of fuel; otherwise incomplete combustion and carbon build up will ultimately damage the engine. Many enthusiasts refer to vegetable oil used as fuel as waste vegetable oil (WVO) if it is oil that was discarded from a restaurant or straight vegetable oil (SVO) to distinguish it from biodiesel.

2.2 Solvent

Actually, there are many types of alcohols such as methanol and ethanol that can be used in the transesterification. Short-chain alcohols such as methanol, ethanol, and butanol are the most commonly used as a solvent. Therefore, selection of the alcohol is depends on cost and performance consideration. Ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols. For example, if methanol is used, the resulting biodiesel is fatty acid methyl ester (FAME), which has proper viscosity, boiling point and high cetane number [Gryglewitz;1999]. But, methanol is the most common alcohol because of it has lower price compared to other alcohols. Handling methanol might be considered an exception to that generality. However, ethanol, as extraction solvent, is preferable to methanol for the transesterification of vegetables oils because of its much higher dissolving power for oils. Therefore, producing ethyl esters rather than methyl esters is of considerable interest, because, in addition to the entirely agricultural nature of the ethanol, the extra carbon atom brought by the ethanol molecule slightly increases the heat content and the cetane number. Finally, another important advantage in the use of ethanol is that the ethyl esters have cloud and pour points that are lower than the methyl esters. This fact improves the cold start.